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## (54) INORGANIC PARTICLE, PHOTSENSITIVE PASTE AND PRODUCTION OF PLASMA DISPLAY

## (57)Abstract:

PROBLEM TO BE SOLVED: To obtain inorganic particles used for producing photosensitive pastes useful the production of plasma display panels each having a high aspect ratio and a highly minute bulkhead and enabling excellent contrast display, by specifying a stimulus value Y in a XYZ color system before calcination and a stimulus value Y after the calcination.

SOLUTION: The inorganic particles have a stimulus value Y of 20-80 before calcination and a stimulus value Y of 5-30 after the calcination. The inorganic particles consist mainly of glass powder (50-90 wt.%), and preferably has an average refractive index of 1.5-1.7, a glass transition point of 450-550° C and a softening point of 500-600° C. The glass powder comprises 3-15 wt.% of lithium oxide, 10-30 wt.% of silicon oxide, 20-40 wt.% of boron oxide, 2-15 wt.% of barium oxide, and 10-25 wt.% of aluminum oxide. The inorganic particles further contain 3-20 wt.% of a black pigment (a metal such as Ru or its oxide) and 10-50 wt.% of a filler (titanium oxide, alumina, etc.).

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 CLAIMS
 

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[Claim(s)]

- [Claim 1] The non-subtlety particle characterized by being a non-subtlety particle for a photosensitive paste, and for the stimulus values Y in the XYZ color system before baking being 20-80, and the stimulus values Y after baking being 5-30.
- [Claim 2] The non-subtlety particle according to claim 1 characterized by containing a black pigment.
- [Claim 3] The non-subtlety particle according to claim 1 or 2 to which it is a kind at least and said black pigment is characterized by the thing as which it was chosen out of the metals or those oxides of Ru, Mn, nickel, Cr, Fe, Co, and Ti, and which is contained three to 20% of the weight in total.
- [Claim 4] A non-subtlety particle given in claim 1 characterized by for a principal component being glass powder and the average refractive indexes of this glass powder being 1.5-1.7 - 3 any 1 terms.
- [Claim 5] The non-subtlety particle according to claim 4 to which said glass powder is characterized by being 450-550 degrees C of glass transition points, and 500-600 degrees C of softening temperatures.
- [Claim 6] The non-subtlety particle according to claim 4 or 5 characterized by said glass powder consisting of a presentation of the following [ the account of an oxide conversion chart ].  
Lithium oxide : 3 - 15-% of the weight oxidation silicon : 10 - 30-% of the weight oxidation boron : 20 - 40-% of the weight barium oxide : 2 - 15-% of the weight aluminum oxide : It is [Claim 7] ten to 25% of the weight. A non-subtlety particle given in claim 1 characterized by containing a filler for the glass powder which is 450-550 degrees C of glass transition points, and 500-600 degrees C of softening temperatures ten to 50% of the weight 50 to 90% of the weight - 6 any 1 terms.
- [Claim 8] The non-subtlety particle according to claim 7 characterized by the thing for which said filler was chosen from the group which consists of titanium oxide, an alumina, barium titanate, a zirconia, cordierite, a mullite, and high-melting glass powder, and which is a kind at least.
- [Claim 9] The non-subtlety particle according to claim 8 characterized by said high-melting glass powder consisting of a presentation of the following [ the account of an oxide conversion chart ].  
Oxidation silicon : 15 - 50-% of the weight boron oxide : 5 - 20-% of the weight aluminum oxide : 15 - 50-% of the weight barium oxide : It is [Claim 10] two to 10% of the weight. The photosensitive paste characterized by being a photosensitive paste containing a non-subtlety particle and a photosensitive organic component, and for the stimulus values Y in the XYZ color system at the time of forming the spreading film with a thickness of 50 micrometers being 20-60, and the stimulus values Y after calcinating this spreading film being 2-20.
- [Claim 11] The photosensitive paste according to claim 10 characterized by the total light transmission of the spreading film with a thickness [ said ] of 50 micrometers being 30% or more.
- [Claim 12] The photosensitive paste according to claim 10 or 11 characterized by for the total reflection factor of the front face of the spreading film with a thickness [ said ] of 50 micrometers being 10% or less, and a normal reflection factor being 50% or more.
- [Claim 13] A photosensitive paste given in claim 10 to which said photosensitive organic component uses a photosensitive monomer, photosensitive oligomer, or a polymer as a principal component, and is characterized by containing a photopolymerization initiator - 12 any 1 terms.
- [Claim 14] The photosensitive paste according to claim 13 characterized by containing the ultraviolet ray absorbent which has an absorption-maximum value to a field with a wavelength of 350-400nm.
- [Claim 15] The photosensitive paste according to claim 14 characterized by the thing for which the ultraviolet ray absorbent was chosen from the group of an azo system color, a benzophenone system compound, a cyanoacrylate system compound, a benzotriazol system compound, and the Indore system compound, and which is a kind at least.
- [Claim 16] A photosensitive paste given in any 1 term of claims 10-15 characterized by containing an ultraviolet ray absorbent 0.1 to 2% of the weight to a non-subtlety particle.
- [Claim 17] A photosensitive paste given in claim 10 characterized by being an object for pattern formation in a plasma display or a plasma-address-liquid-crystal display - 16 any 1 terms.
- [Claim 18] By applying and drying on a substrate the non-subtlety particle whose stimulus values Y in the XYZ color system before baking are 20-80 and whose stimulus values Y after baking are 5-30, and the photosensitive paste containing a photosensitive organic component The manufacture approach of the plasma display which carries out patterning by the photolithography method and is characterized by calcinating this pattern and the stimulus value Y in an XYZ color system forming the septum of 2-20 after the stimulus value Y in an XYZ color system forms the spreading film of 20-60.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of the non-subtlety particle and the photosensitive paste which are used for production of the septum of a plasma display or a plasma-address-liquid-crystal display, and a plasma display.

[0002]

[Description of the Prior Art] Since a high-speed display is possible for a plasma display panel (it considers as Following PDP) compared with a liquid crystal display and it is easy to enlarge, it has permeated fields, such as OA equipment and a public-relations display. Moreover, progress of the field of a high definition television etc. is expected very much.

[0003] With expansion of such an application, it is minute and the color PDP which has many display cells attracts attention. PDP makes the anode and the cathode inter-electrode which counter in the discharge space prepared between the front-windshield substrate and the tooth-back glass substrate produce plasma discharge, and displays by hitting to the fluorescent substance which established the ultraviolet rays generated from the gas enclosed in this discharge space in discharge space. In this case, at the same time it presses down the breadth of discharge to a fixed field and makes a display perform within a regular cell, and in order to secure uniform discharge space, the septum (it is also called an obstruction and a rib) is formed.

[0004] The septum in PDP was calcinated and formed after making it predetermined height by repeating the process of printing an insulating glass paste in the shape of a pattern with screen printing, and drying from the former, 5 to about ten times. However, especially in screen printing, when panel size is enlarged, there is a problem that the alignment of the discharge electrode and the printing location of an insulating glass paste which are beforehand formed on the substrate is difficult, and location precision is hard to be acquired. And in order to obtain predetermined septum height, by performing many superposition printings, flapping of a septum and its side-face edge section and turbulence of the skirt arise, and there is a fault from which the precision of height is not acquired. Moreover, there is a problem from which a septum becomes neither a rectangle nor a trapezoid cross-section configuration. For this reason, high definition septum formation is difficult, display quality worsens, and troubles, such as being low, also have a yield with bad workability.

[0005] Furthermore, with large-area-izing of PDP, and high-resolution-izing, by the approach by such screen-stencil, manufacture of a high aspect ratio and a high definition septum becomes difficult technically, and it is becoming in cost and disadvantageous.

[0006] In JP,1-296534,A, JP,2-165538,A, JP,5-342992,A, and JP,6-295676,A, the approach of forming a septum with a photolithography technique, using a photosensitive paste as an approach of improving this problem is proposed. Furthermore by JP,8-50811,A, the approach of forming a septum by one exposure is proposed using photosensitive glass mull technique. However, by these approaches, since the septum was white, when using for PDP and a plasma-address-liquid-crystal display, there was a problem that contrast ran short.

[0007] That is, after pattern processing is carried out using an insulating glass paste or a photosensitive paste, it is calcinated and the septum for PDP is formed. However, although it was effective in the improvement in brightness since there was a light reflex from a septum at the time of luminescence when this septum was white, there was a problem that contrast fell for the outdoor daylight reflection at the time of un-emitting light from a septum top face.

[0008] On the other hand, in order to raise pattern resolution, the manufacture approach of the septum using the photosensitive paste containing a black pigment is proposed by JP,6-144871,A and JP,8-17345,A. However, the hardening depth obtained by one exposure was insufficient for the black pigment in order to absorb light, and it had the problem for which many exposure is needed. About the improvement in contrast depended black whenever the septum furthermore obtained is black, it is not taken into consideration at all.

[0009] Moreover, in order to improve contrast, the panel structure which forms a black septum on a front-windshield substrate was also proposed, but since it was necessary to form separately the black septum of that it is necessary to perform alignment of the septum of a front-windshield substrate and a tooth-back glass substrate, and a front-windshield substrate, and the white septum of a tooth-back glass substrate, there was a fault to which a process becomes complicated. Furthermore, screen printing is used as the formation approach of a septum, and there was a problem of being unable to form with a sufficient precision.

[0010]

[Problem(s) to be Solved by the Invention] Then, this invention has a high aspect ratio and high definition septum, and sets it as the purpose to offer the non-subtlety particle for manufacturing PDP in which the display which was excellent in contrast is possible, a photosensitive paste, and the manufacture approach of PDP.

[0011]

[Means for Solving the Problem] The non-subtlety particle characterized by being a non-subtlety particle for a photosensitive paste, and for the stimulus values Y in the XYZ color system before baking being 20-80, and the stimulus values Y after baking being 5-30 can attain the purpose of this invention.

[0012] Moreover, the photosensitive paste of this invention which used the above-mentioned inorganic particle is a photosensitive paste characterized by being a photosensitive paste containing a non-subtlety particle and a photosensitive organic component, and for the stimulus values Y in the XYZ color system at the time of forming the spreading film with a thickness of 50 micrometers being 20-60, and the stimulus values Y after calcinating this spreading film being 2-20.

[0013] The manufacture approach of PDP of this invention using the above-mentioned inorganic particle and a photosensitive paste By applying and drying on a substrate the non-subtlety particle whose stimulus values Y in the XYZ color system before baking are 20-80 and whose stimulus values Y after baking are 5-30, and the photosensitive paste containing a photosensitive organic component After the stimulus value Y in an XYZ color system forms the spreading film of 20-60, it is the manufacture approach of PDP which carries out patterning by the photolithography method and is characterized by calcinating this pattern and the stimulus value Y in an XYZ color system forming the septum of 2-20.

[0014]

[Embodiment of the Invention] Hereafter, this invention is stated to a detail.

[0015] As described above, in order to manufacture PDP which has a high aspect ratio and high definition septum, it is desirable to use the photolithography method for formation of a septum pattern. That is, it is the approach of irradiating ultraviolet rays etc. and forming a septum pattern in the photosensitive paste coating film.

[0016] Therefore, as for the phase, the non-subtlety particle which it goes back further and is the principal component of a photosensitive paste, and the photosensitive organic component of the photosensitive paste coating film, it is desirable that it is the component which often penetrates ultraviolet rays. In other words, in the phase of a non-subtlety particle and the photosensitive paste coating film, it is desirable that they are white or gray. In order [ the ] to raise the contrast of PDP on the other hand, the black thing of a septum is desirable.

[0017] Then, when this invention makes the specific range the stimulus value Y in the XYZ color system before and behind baking of a non-subtlety particle, it is [ value / Y / before and behind baking of the photosensitive paste containing this non-subtlety particle / stimulus ] high in light transmission nature before baking, and after baking makes it possible to black-ize it, if it is low and light transmission nature is put in another way. Therefore, even if an exposure process is once by applying this photosensitive paste on a substrate, exposing this, and forming and calcinating a septum pattern, the black-ized suitable septum for the improvement in contrast of PDP can be formed with a high aspect ratio and a high definition.

[0018] As a result of this invention persons' examining wholeheartedly PDP which was excellent in contrast, it became clear that it is effective to set the stimulus value Y in the XYZ color system of a septum to 2-20. Whenever [ black ] has the too high stimulus value Y at less than two, the effect of almost reflection is lost, and a display property falls. Moreover, if the stimulus value Y exceeds 20, it will come to wear gray and contrast and color purity will fall. Furthermore, it turned out that x at the time of asking for a chromaticity coordinate x and y and the value of y can improve the color purity of the luminescent color of a plasma display by making it 0.3-0.36, respectively based on the tristimulus value XYZ.

[0019] so, as a result of repeating research further, in order to form the septum whose stimulus values Y in an XYZ color system are 2-20 and a chromaticity coordinate x and whose y are 0.3-0.36, respectively The stimulus values Y after baking of the non-subtlety particle which constitutes a septum need to be 5-30. and in order to maintain the light transmission nature of the paste coating film required while having the above-mentioned stimulus value Y, in order to form a high aspect ratio and high definition septum by exposure once before baking It found out that the stimulus values Y of the non-subtlety particle before baking and a photosensitive paste needed to be 20-80, and 20-60, respectively.

[0020] If the stimulus value Y of a non-subtlety particle and a photosensitive paste exceeds 80 and 60, respectively, whenever [ of the septum after baking / black ] will run short, and the contrast of PDP will fall. Moreover, the ultraviolet-rays permeability of the paste coating film falls [ the stimulus value Y of a non-subtlety particle and a photosensitive paste ] less than by 20, and since the photoreaction to the lower part of the spreading film does not fully advance, pattern formation nature falls. It is especially desirable that the stimulus values Y of a non-subtlety particle are 30-60.

[0021] Moreover, whenever [ black ] is too high in the stimulus value Y of the non-subtlety particle after baking being less than five, the display property of PDP falls, if the stimulus value Y exceeds 30, it will come to wear gray and the contrast and color purity of PDP will fall.

[0022] In addition, the chromaticity coordinate x and y which are called for from the tristimulus value XYZ of the self-luminous color and them in this invention are JIS. Z8722 (measuring method of the object color), JIS Z8717 (measuring method of the fluorescence object color), JIS It considers as the value calculated by the approach specified to Z8701 (the color specification approach by the XYZ color system and 10Y10ZX10 color coordinate system).



[0023] Specifically, measurement of Y value and a chromaticity coordinate x, and y was performed about the septum which calcinated the powder, the photosensitive paste coating film, and spreading film of a non-subtlety particle, and was formed by the following approaches.

[0024] A measuring method concrete as an example is first shown for a septum.

[0025] The test portion applied the photosensitive paste to the desiccation thickness of 50 micrometers on 80mm angle and the soda glass substrate with a thickness of 1.3mm, and at 580 degrees C, this was calcinated for 30 minutes and it produced it. It measured using this solid film baking sample, using a white plate (the thing of a barium sulfate, X= 91.06, Y= 93.01, and Z= 106.90 being used as a reference standard) as two C light (\*\*\*\*\*) visual field and criteria. In advance of measurement, zero-point doubling was performed for the white plate only to the soda glass substrate in the sample base in piles. A test portion makes a baking sample side the optical direction of radiation, establishes it in the sample base which has the measurement hole of 12mmphi, and put the white plate on the glass substrate side in piles. The location of a test portion is changed, and measurement of three points is performed, and let the average be the measured value of Y value. The value of x and y is calculated by count.

[0026] The measurement about the photosensitive paste coating film was measured in the condition before baking according to the above, and about the non-subtlety particle, what filled up the transparent bag with the non-subtlety particle was treated like the spreading film or a septum layer, and it measured it.

[0027] The stimulus value and the chromaticity coordinate were measured using color computer SM-7-CH (optical condition 45-degree lighting, 0-degree light-receiving) by Suga Test Instruments Co., Ltd.

[0028] Below, the non-subtlety particle of this invention is described further.

[0029] Although this invention persons have done various researches about the pattern formation nature of the photosensitive paste which uses a non-subtlety particle and a photosensitive organic component as a principal component It is sharp, it is required to make the ultraviolet rays used for pattern exposure penetrate in [ as possible ] rectilinear propagation, in order to form the pattern which was excellent in the configuration, and it has found out that one of the effective factors for it is adjusting the average refractive index of a non-subtlety particle and a photosensitive organic component.

[0030] It is desirable that the principal component of a non-subtlety particle is glass powder in this invention, and the average refractive indexes of this glass powder are 1.5-1.7 from this point. If it is in this range, adjustment with the average refractive indexes 1.45-1.7 of a photosensitive organic component is good, and can form the septum pattern of a desired configuration easily.

[0031] Moreover, since glass powder is sintered at a baking process, and forms a septum and baking is performed on a glass substrate, they are the conditions which need not making substrate glass transform. It is desirable that they are 450-550 degrees C of glass transition points of this point to glass powder and 500-600 degrees C of softening temperatures. It considers as the glass powder with which are satisfied of both the range of these heat characteristics and the above-mentioned average refractive index, and what consists of the following presentations in the account of an oxide conversion chart is mentioned preferably.

[0032]

Control of glass softening temperature and a coefficient of thermal expansion not only becomes easy, but it can make the average refractive index of glass low by using the glass powder which contains lithium oxide three to 15% of the weight in the above-mentioned presentation lithium oxide ten to 25% of the weight. : 3 - 15-% of the weight oxidation silicon : 10 - 30-% of the weight boron oxide : 20 - 40-% of the weight barium oxide : 2 - 15-% of the weight aluminum oxide : Also in order for an addition to raise the stability of a paste, 15 or less % of the weight is desirable, and is 10 % of the weight more preferably.

[0033] It is desirable to blend oxidation silicon in 10 - 30% of the weight of the range, when it is less than 10 % of the weight, compactness, and the reinforcement and stability of a glass layer fall, and a coefficient of thermal expansion separates from a desired value, and a mismatch with a glass substrate tends to happen. Softening temperature becomes high and it becomes impossible that it will be hard to be burned on a glass substrate if 30 % of the weight is exceeded.

[0034] As for boron oxide, it is desirable to blend in 20 - 40% of the weight of the range. If it exceeds 40 % of the weight, the stability of glass will fall. A strong fall and the fall of the stability of glass take place at less than 20 % of the weight.

[0035] Although the barium oxide is used at 2 - 15 % of the weight, it becomes difficult to control glass baking temperature and electric insulation by less than 2 % of the weight. Moreover, if it exceeds 15 % of the weight, the stability and compactness of a glass layer will fall.

[0036] Although an aluminum oxide is used at 10 - 25 % of the weight, a point [ distortion ] is raised or it is added for stabilization of a glass presentation, or pot-life extension of a paste. At less than 10 % of the weight, if the reinforcement of a glass layer falls and it exceeds 25 % of the weight, the heat-resistant temperature of glass will become high too much, and baking will become difficult on a glass substrate. Moreover, a precise insulating layer becomes that it is hard to be obtained at the temperature of 600 degrees C or less.

[0037] A zinc oxide, a calcium oxide, or a magnesium oxide may be contained with the oxide notation other than these components.

[0038] As for a zinc oxide, it is desirable to be contained in 2 - 15% of the weight of the range. At less than 2 % of the weight, there is no effectiveness in the improvement in compactness of an insulating layer. If 15 % of the weight is exceeded, since the temperature carried out by the ability being burned on a glass substrate will become low, and it will be hard coming to control and insulation resistance will become low, it is not desirable.

[0039] Although a coefficient of thermal expansion is controlled, a calcium oxide is added while it makes glass easy it to be desirable to be contained in 2 – 13% of the weight of the range, and to fuse. If fewer than 2 % of the weight, a point [ distortion ] will become low too much.

[0040] Although a coefficient of thermal expansion is controlled, a magnesium oxide is added while it makes glass easy it to be desirable to be contained in 1 – 15% of the weight of the range, and to fuse. Glass becomes easy to devitrify and is not desirable if 15 % of the weight is exceeded.

[0041] Moreover, although titanium oxide, a zirconium dioxide, etc. can be contained in glass powder, as for the amount, it is desirable that it is less than 5 % of the weight. A zirconium dioxide has effectiveness in controlling the softening temperature, the transition point, and electric insulation of glass.

[0042] As for the non-subtlety particle of this invention, it is desirable 50 – 90 % of the weight of glass powder which has the above-mentioned glass transition point and softening temperature, and that high-melting glass, the ceramics, etc. are included ten to 50% of the weight as a filler.

[0043] By addition of these filler components, contraction at the time of baking becomes small, and the configuration holdout and precision of a septum pattern improve. Furthermore, these filler addition is desirable when maintaining the reinforcement of the obtained septum. When a filler forms a septum with a photosensitive paste at less than 10 % of the weight, burning shrinkage is made low or there is no effectiveness which controls a coefficient of thermal expansion. On the other hand, when the content of a filler exceeds 50 % of the weight, it becomes what is inferior in the septum after baking in respect of compactness, and a septum becomes low strength, a septum may separate or the defect of dropping out may occur. Moreover, it may become the cause which adsorption and the organic component of minute amount moisture remain, and causes the fall of a discharge property into a septum.

[0044] it was chosen out of the group which consists of titanium oxide, an alumina, barium titanate, a zirconia, cordierite, a mullite, and high-melting glass powder as a filler — a kind can be used at least. It is desirable at a point with high-melting glass powder able to control an average refractive index, softening temperature, and a coefficient of thermal expansion by modification of a presentation about especially.

[0045] As high-melting glass powder, a 650–800-degree C thing is desirable, and although it also consists of the following presentations in the account of an oxide conversion chart, it is [ 550–1200 degrees C of softening temperatures ] still more preferably desirable.

[0046]

Oxidation silicon : 15 – 50-% of the weight boron oxide : 5 – 20-% of the weight aluminum oxide : 15 – 50-% of the weight barium oxide : Especially two to 10% of the weight, it is desirable in high-melting glass powder to contain oxidation silicon and an aluminum oxide 15% of the weight or more, respectively, and it is effective in it that these content sum totals are 50 % of the weight or more among high-melting glass powder in order to give a required heat characteristic.

[0047] As for high-melting glass powder, it is still more desirable that 0.4–2 micrometers and D50 are [ 1–3 micrometers and D90 ] 3–8 micrometers and the maximum particle diameter of 10 micrometers or less for D10. D10, D50, and D90 are the particle size of the powder of ten volume %, 50 volume % (mean particle diameter), and 90 volume % from powder with a respectively small particle size here.

[0048] It is desirable, when the particle size distribution of high-melting glass powder is in the above-mentioned range, burning shrinkage can be made low and the septum of low porosity is produced.

[0049] If the bigger powder as high-melting glass powder than the above-mentioned particle size is used, since porosity not only rises, but the irregularity of a septum crowning may be expanded and discharge may be caused, it is not desirable.

[0050] In addition, it mixes so that it may become a predetermined combination presentation, high-melting glass powder is quenched after melting at 900–1400 degrees C, after making it into a glass frit, it is ground, and it is used as a thing of the above-mentioned particle size distribution.

[0051] As for the refractive index of a filler component, it is desirable that it is 1.5–1.8, and 1.5–1.68 are more desirable. Since it will become easy to have consistency with the average refractive index of the photosensitive organic component under photosensitive paste and will contribute to the improvement in light transmission of a photosensitive paste (prevention of dispersion or reflection) if the rate of leading of a filler component is in this range, highly precise pattern formation becomes easy.

[0052] Moreover, when the refractive index of  $n_1$  and a filler component is set to  $n_2$  for the average refractive index of the above mentioned glass powder, it is desirable to fill the relation of  $-0.05 \leq n_1 - n_2 \leq 0.05$ . If the refractive-index difference of glass powder and a filler component is in this range, since index matching with a photosensitive organic component will become easier and septum pattern formation nature will improve, it is desirable.

[0053] As described above, in the phase of a non-subtlety particle and the photosensitive paste coating film, the description of this invention is white or gray, and after it calcinates a septum pattern, it is to be able to obtain the septum in which whenever [ sufficient / black ] is shown. It is indispensable conditions that the photosensitive paste coating film is white or gray, in order to make the ultraviolet rays irradiated for pattern formation penetrate to the lower part of the spreading film and to carry out photo-curing enough. Although the photosensitive paste coating film containing the non-subtlety particle of this invention satisfies this condition and a non-subtlety particle shows white or gray in the photosensitive paste phase before baking, it is desirable that it is necessary to black-ize after baking, and for that a black pigment is included.

[0054] As a desirable black pigment, the metals or those oxides of Ru, Mn, nickel, Cr, Fe, Ti, and Co are mentioned, and these things [ containing a kind three to 20% of the weight in total at least ] are desirable. Although light will be

scattered about for the shape of powder and white or gray will be presented in the state of a non-subtlety particle if the above-mentioned metal or some kinds of those oxides contain in a non-subtlety particle, although the detail of the device black-ized after baking is not clear, the electronic state (electronic valence) of the black pigment which is contained in a non-subtlety particle in the process calcinated and which mainly consists of a transition-metals element changes. For this reason, the band condition of d electron which absorbs the light comes to change, and is presumed to black-ize. Furthermore, it is desirable to use it for red, green, and blue combining three kinds of black pigments colored each after baking, and to use a black septum as neutral black.

[0055] What is necessary is just to mix the above-mentioned black pigment, in case glass powder and a filler are mixed and a non-subtlety particle is manufactured in order to make it act as a black pigment. Moreover, it is also desirable to use the powder which added the black pigment, and fused and produced it in the manufacture process of glass powder. In the case of the powder which carried out melting mixing, since a black pigment is dissolved in homogeneity and homogeneity, control of the particle size distribution of the glass powder after grinding becomes easy. Moreover, the addition of a black pigment is also little compared with the case where glass powder is mixed in the state of powder, and since a black septum without homogeneous nonuniformity is obtained, it is desirable.

[0056] although one kind of the simple above-mentioned metal mixed and melting mixed or its oxide may not come out and two or more sorts may be used for it, since it is excellent in controlling whenever [ of functional maintenance of a photosensitive paste, and the septum obtained / black ] that it is 3 – 20 % of the weight in total, it is desirable. It is 5 – 15 % of the weight more preferably. At less than 3 % of the weight, whenever [ of a septum / black ] becomes weak, it is visible to gray, and there is little improvement effectiveness in contrast. Moreover, if [ than 20 % of the weight ] more, the softening temperature of glass will go up or it will become difficult to adjust a coefficient of thermal expansion with a glass substrate.

[0057] As a non-subtlety particle of this invention, they are the average refractive indexes 1.5–1.7. The glass transition point 450–550 degrees C, A kind of filler chosen from the glass powder, the high-melting glass, or the ceramics characterized by containing the lithium oxide whose softening temperature is 500–600 degrees C is included at least. What contains in total the component chosen from the metals or those oxides of Ru, Mn, nickel, Cr, Fe, Ti, and Co three to 20% of the weight is mentioned especially preferably.

[0058] Moreover, since the non-subtlety particle of this invention is an object for a photosensitive paste, into a photosensitive organic component, it carries out distributed mixing and is used. Therefore, in addition to the above-mentioned conditions, homogeneity distribution is carried out into a photosensitive organic component, and moreover, if restoration nature is not good, the good paste of pattern formation nature cannot be obtained. Therefore, the particle size and distribution of a non-subtlety particle serve as important requirements.

[0059] this invention persons by using for a photosensitive paste the glass powder with which particle size distribution have at least two peaks, when the histogram with which the axis of ordinate was made into frequency(%), and it already made the axis of abscissa particle size (micrometer) shows the particle size distribution of glass powder When the spreading film of a paste was formed, light scattering in the film was controlled, and total light transmission is high, it has found out that the photosensitive paste in which the outstanding pattern property is shown can be obtained, and it is desirable to satisfy such particle size distribution.

[0060] The glass powder used as a principal component of the non-subtlety particle of this invention is produced through the process of preparation of for example, a preparation raw material, melting, grinding, classification, and desiccation. The particle size distribution of glass powder are controlled in the above-mentioned grinding and a classification process. As for grinding, the approach of a ball mill, a jet mill, etc. is used, and a classification is sifted out and performed by dry classification, such as an air-current type classification.

[0061] In addition, the particle size distribution of a non-subtlety particle and glass powder can be measured by the laser diffraction scattering method. For example, the Measuring condition at the time of using micro truck company make and particle-size-distribution meter HRA9320-X100 is as follows.

[0062]

The amount of samples : 1g distribution conditions : It is ultrasonic distribution for 1 – 1.5 minutes in purified water. When it is hard to distribute, it carries out in 0.2% hexametaphosphoric acid sodium water solution.

[0063]

Particle refractive index: Change according to the class of glass (in the case of a lithium system 1.6).

Solvent refractive index: 1.33 measurement sizes : More nearly twice to a general one, the thing which has a small particle size tends to condense powder, when homogeneity does not distribute but the spreading film is formed during a paste, since an opening becomes easy to be made, light transmission nature becomes low, and a desired pattern property is not acquired. On the other hand, if particle size is too large, depending on burning temperature, irregularity arises in the crowning of the septum after baking, a clearance will be made between front plates at the time of sealing, and a cross talk will arise. As a result of the wholeheartedly examination about these troubles, the mean particle diameter (D50) of glass powder had coherent [ little ] as it is 1.5–7 micrometers and the maximum particle diameter is 7–40 micrometers, since restoration nature was good, it was possible to have obtained the paste which was excellent in pattern formation nature, and since there was neither irregularity of the septum crowning after baking nor a problem of a foreign matter further, it found out that it was suitable for highly minute septum formation.

[0064] Coherent [ powdered ] is large in mean particle diameter being less than 1.5 micrometers, and there is an inclination for pattern formation nature to fall. If larger than 7 micrometers, since the irregularity of the septum crowning after baking will become large, a cross talk may occur at the time of discharge. 1.5–7 micrometers of mean



particle diameter are 2–6 micrometers preferably.

[0065] Moreover, in less than 7 micrometers, restoration nature has the bad maximum particle diameter, and there is an inclination for pattern formation nature to fall. If 40 micrometers is exceeded, a foreign matter will remain in the irregularity of the septum crowning after baking, or discharge space. The maximum particle diameter is desirable in order that that it is 10–30 micrometers may control more preferably 7–40 micrometers of irregularity of powdered restoration nature or a septum crowning.

[0066] Coherent can obtain little good glass powder of restoration nature as D10 of glass powder is 0.5–2 micrometers and D90 is 4–20 micrometers. Coherent [ of glass powder ] is high in D10 being less than 0.5 micrometers, and it is hard to obtain a high definition pattern by dispersion by the opening between the condensed particles. When 2 micrometers is exceeded, since the yield at the time of classification worsens or the irregularity of the septum crowning after baking becomes large, a cross talk may arise. D10 is desirable at the point whose powdered yield that it is 0.7–1.5 micrometers controls more preferably 0.5–2 micrometers of powdered condensation, and improves.

[0067] In less than 4 micrometers, since restoration nature worsens, D90 has the inclination for pattern formation nature to fall. When 20 micrometers is exceeded, a foreign matter may remain in the irregularity and discharge space of a septum crowning. 4–20 micrometers, as for D90, it is preferably desirable that it is 6–15 micrometers in order to control the irregularity of the restoration nature of glass powder, or a septum crowning.

[0068] Moreover, the tap density of glass powder can have good restoration nature in 0.6g /or more being [ cc ] 0.65g/cc or more more preferably, and its pattern formation nature of a paste can improve, and it can perform high definition septum formation. Tap density is JIS. Setting to this invention which is the mass per unit volume of the powder in the container which vibrated Z2500 (2045) as the publication, tap density is TSUTSUI. SCIENTIFIC INSTRUMENTS Co.A.B.D POWDER After vibrating 100 cc container into which glass powder was put for 5 minutes using TESTER, glass powder had been printed, and the mass per 100 cc was measured and obtained.

[0069] The non-subtlety particle of this invention can be manufactured by, for example, mixing suitably the above-mentioned glass powder, a filler, and a black pigment.

[0070] Next, a photosensitive paste is explained. The photosensitive paste of this invention consists of the non-subtlety particle and the photosensitive organic component which satisfy the conditions of the above-mentioned stimulus value Y, and a septum pattern is formed, and it is used in order to calcinate it and to create a septum. The stimulus values [ in / in a photosensitive paste / the XYZ color system of the spreading film of 50 micrometers of thickness ] Y need to be 20–60, and the stimulus values Y after calcinating this spreading film need to be 2–20. If the stimulus value Y in the XYZ color system of the photosensitive paste coating film is in this range, transparency of ultraviolet rays cannot be barred, but light exposure can be set as two or less 500 mJ/cm, and a tact time can be lowered. The configuration of the obtained septum pattern is also excellent.

[0071] The stimulus value Y in the XYZ color system before baking which was described above can show 20–80, the conditions of the stimulus value Y of the photosensitive paste described above by containing as a component the non-subtlety particle of this invention whose stimulus values Y after baking are 5–30 can be satisfied easily, and the stimulus value Y in an XYZ color system can obtain the septum of 2–20.

[0072] In addition, the photosensitive paste with which the stimulus value Y in an XYZ color system consists of a non-subtlety particle of the white of 20–80 – gray and an almost transparent photosensitive organic component is influenced of the minute amount addition component for raising the pattern formation nature of a paste etc., and, for this reason, the stimulus value Y of a photosensitive paste changes to the range of 20–60. Less than by 20, ultraviolet rays will be absorbed with the spreading film of a photosensitive paste, and the stimulus value Y does not fully carry out photo-curing to the lower part (light transmission falls). For this reason, pattern formation nature worsens. Moreover, if the stimulus value Y exceeds 60, whenever [ of the septum after baking / black ] will fall and a contrast improvement effect will become inadequate. It is 30–50 more preferably.

[0073] In addition, the stimulus value Y of the need of being 2–20 after baking of the spreading film of 50 micrometers of thickness of a photosensitive paste is the same as that of a septum, whenever [ black ] has the too high stimulus value Y at less than two, and the display property of PDP falls. Moreover, if the stimulus value Y exceeds 20, it will come to wear gray and the contrast and color purity of PDP will fall.

[0074] Moreover, in order that the light transmission of a photosensitive paste may do effect important for the pattern formation nature of a paste, as for a photosensitive paste, it is desirable that the total light transmission measured by 50 micrometers of thickness is 30% or more, and it is 50% or more more preferably. It is desirable that the total light transmission measured in g line wavelength field which has a role important for pattern formation especially is 50% or more more preferably 30% or more.

[0075] As for the photosensitive paste of this invention, it is still more desirable that the normal permeability which is described below in addition to the total light transmission of the spreading film of 50 micrometers of thickness being 30% or more is 30% or more and 50 more% or more. That is, it is desirable that there are many amounts of beams of light which penetrate a photosensitive paste, and it is desirable that the rate of the light further penetrated in rectilinear propagation among the beam of light to penetrate is high.

[0076] It is important to satisfy this requirement, when performing pattern processing of a high aspect ratio. In order to obtain such total light transmission, it is important to use a component with high light transmission for the non-subtlety particle and the photosensitive organic component which constitute a photosensitive paste, and to mix this to homogeneity. Furthermore, it is required to adjust the average refractive index of a non-subtlety particle and each photosensitive organic component as much as possible.

[0077] In addition, measurement of light transmission was performed using the spectrophotometer (the Shimadzu make, UV-3101PC). The Measuring condition is as follows.

[0078]

sample path length: — 50-micrometer sample cell: — quartz slit width: — 7.5nm reading-per-second: — SLOW (about 100 nm/min)

light source: — halogen lamp measurement wavelength: — 360-850nm white sheet: — BaSO<sub>4</sub> (sample side)

A subwhite sheet: BaSO<sub>4</sub> (reference side)

angle-of-incidence: — 0 times sample room: — a multipurpose large-sized sample room unit (Shimadzu PC-3100 mold)

integrating-sphere: — 60phi integrating-sphere integrating-sphere aperture: — inlet-port aperture 12(W) x20(H) mm outlet aperture 12(W) x24(H) mm phot mull aperture (under ball): — 16mmphi PbS cell aperture (on ball): — rate [ of 16mmphi integrating sphere ] of throat area ratio: — 12.9% detector: — phot mull And PbS-cell data processing: On MCB17JH20/PC9801 quartz cell, put a quartz cell from on a sample and adjust a measurement sample, after applying a photosensitive paste so that the thickness after desiccation may be set to 50 micrometers. On the above-mentioned specification and conditions, after measuring the total light transmission T1, as the part (white sheet: part attached in an outlet aperture) which measures the rectilinear-propagation light of an integrating sphere was removed and light of rectilinear-propagation light was not detected, the luminous diffuse transmittance T2 (light penetrated without going straight on by dispersion etc. comparatively) was measured. A luminous diffuse transmittance (T2) is deducted from total light transmission (T1), and value T3= (T1-T2) which \*(ed) this with total light transmission / T1 is called normal permeability (it is also called rectilinear-propagation permeability).

[0079] The total reflection factor in the front face of the spreading film of 50 micrometers of thickness of the photosensitive paste of this invention is 10% or less, and a normal reflection factor is [ the total reflection factor ] more preferably [ 50% or more of ] more desirable still 20% or more.

[0080] Reflection factor measurement of the spreading film is performed using the same spectrophotometer as transmissometry. The total reflection factor (Rt) measures the total reflection of the light which carried out incidence by eight incident angles here. The reflection factor of the diffusion component which furthermore carried out incidence by zero incident angle among reflection was measured, and this was made into diffuse reflection (Rd). Rn calculated as (Rt-Rd)/Rt=Rn was made into the normal reflection factor at this time. The barium-sulfate plate was used as a reflecting plate 100%.

[0081] That is, a normal reflection factor is a rate except the total reflection factor to a diffusion component. When carrying out patterning of the photosensitive paste, the light which came out of the exposure light source is adjusted by the reflecting plate of an aligner, is irradiated as a parallel ray, and it passes a photo mask in rectilinear propagation, and it arrives at the front face of the photosensitive paste coating film. The rate of light reflected in accordance with the optical path of an incident ray is a normal reflection factor. Although it is hard to avoid that a part of irradiated light is reflected on a front face, reflection of the exposure light resulting from the front face and surface condition of the spreading film is controlled as much as possible, and, as for the light to reflect, it is desirable to become normal reflection as much as possible.

[0082] Especially the photosensitive paste of this invention is desirable in order that it may make a pattern configuration good that the total reflection factor of the spreading film measures with the light of g line wavelength field, and is 10% or less, and the normal reflection factor is 20% or more.

[0083] The photosensitive organic component which constitutes the photosensitive paste of this invention is explained.

[0084] As for a photosensitive organic component, in this invention, it is desirable that it is the type which the part which used a photosensitive monomer, photosensitive oligomer, or a polymer as the principal component, contains a photopolymerization initiator, and was exposed by optical initiation radical reaction insolubilizes to a developer.

[0085] Although the compound which has an activity carbon-carbon double bond as a photosensitive monomer is mainly used, monofunctional and the multifunctional compound which have a vinyl group, an allyl group, an acrylate radical, a methacrylate radical, an acrylamide radical, etc. are used as a functional group. It is desirable to use a polyfunctional acrylate compound and/or a polyfunctional methacrylate compound especially.

[0086] Moreover, while playing roles formed by the photoreaction as an organic component during a photosensitive paste, such as improvement in the physical properties of a hardened material, and adjustment of the viscosity of a paste, it is common that the oligomer or the polymer which has the function to control the solubility of an unexposed paste is used together. What has the frame of the carbon chain acquired by the polymerization or copolymerization of a component chosen from the compound with which these oligomer or polymers have a carbon-carbon double bond is used. As a monomer to copolymerize, unsaturated carboxylic acid etc. is useful and it can consider as the photosensitive paste which can develop an unexposed part in an alkali water solution after sensitization. In this way, it is desirable 50-160, and to control the acid number of the oligomer or the polymer which has acid radicals, such as a carboxyl group, in the obtained side chain to become the range of 70-140 preferably.

[0087] For using it as photosensitive oligomer or a polymer, the thing of the weight average molecular weight 2000-60,000 which contains a carboxyl group and a partial saturation double bond in intramolecular is desirable. It is 3000-40,000 more preferably. In order to introduce a partial saturation double bond, the method of carrying out the addition reaction of the ethylene nature unsaturated compound and acrylic-acid chloride which have a glycidyl group and an isocyanate radical, and the methacrylic-acid chloride to the oligomer or the polymer which has a carboxyl group in a side chain is applied. the ethylene nature partial saturation which makes photosensitivity the number of

carboxyl groups, the oligomer, or the polymer for alkali water-solution development nature — the base can be freely chosen by the reaction condition.

[0088] the case where the photosensitive paste containing the above photosensitive components is exposed — a photosensitive component — a polymerization — and crosslinking reaction is carried out and it becomes insolubility at a developer. Therefore, a photopolymerization initiator is added as a component which generates an activity radical and starts a radical polymerization and crosslinking reaction. Furthermore, a sensitizer is used with a photopolymerization initiator, sensibility is raised or what (spectral sensitization) (chemical sensitization) and the wavelength range of a light effective in a reaction are expanded for is made. These photopolymerization initiators and sensitizers can be used choosing them from a known compound group.

[0089] It is effective in order to obtain the septum pattern with which adding an ultraviolet ray absorbent excelled [ paste / in which a non-subtlety particle is contained so much / photosensitive ] in the configuration in order to control the unnecessary photoreaction which occurs by the scattered light. The organic system color which has the absorption maximum in the wavelength range of 350–400nm is preferably used for an ultraviolet ray absorbent. specifically, it was chosen out of the group of an azo system color, a benzophenone compound, a cyanoacrylate system compound, a benzotriazol system compound, and the Indore system compound — a kind is mentioned preferably at least.

[0090] Sudan (chemical formula  $C_{24}H_{20}N_4O$ , molecular weight 380.45) which is azo system organic dye as an example, 2, 4-dihydroxy benzophenone, 2-hydroxy-4-methoxybenzophenone, 2, 2'-dihydroxy -4, a 4'-dimethoxy benzophenone, 2, 2'-dihydroxy -4, a 4'-dimethoxy-5-sulfo benzophenone, 2 - Hydroxy-4-methoxy-5-sulfo benzophenone TORIHIDO rate, 2-hydroxy-4-n-octoxybenzophenone, a 2-hydroxy-4-OKUTADE siloxy benzophenone, 2, 2', 4, and 4' — a - tetra-hydroxy benzophenone and a 4-DODESHIROKISHI-2-hydroxy benzophenone — 2-hydroxy-4-(2-hydroxy-3-meta-chestnut ROKISHI) propoxybenzophenone, 2-(2'-hydroxy-5'-methylphenyl) benzotriazol, 2-(2'-hydroxy - 3', 5' -t-butyl -5'-methylphenyl) benzotriazol, 2-(2'-hydroxy-3' -t-butyl -5'-methylphenyl)-5-chlorobenzo triazole, 2-(2' - hydroxy-3', 5'-G t-buthylphenyl)-5-chlorobenzo triazole, 2-(2'-hydroxy-4'-n-octoxy phenyl) benzotriazol, 2-ethylhexyl-2-cyano - 3 and 3-diphenyl acrylate, 2-ethyl-2-cyano - 3 and 3-diphenyl acrylate, BONASORB UV-3901 (the ORIENT chemistry company make), BONASORB Although UA-3902 (the ORIENT chemistry company make), SOM-2-0008 (the ORIENT chemistry company make), etc. can be mentioned It is not limited to these.

[0091] The addition of these ultraviolet ray absorbents has 0.1 – 2 desirable % of the weight to the non-subtlety particle contained during a photosensitive paste. At less than 0.1 % of the weight, since the sensibility of a photosensitive paste will fall if the addition effectiveness of an ultraviolet ray absorbent is not enough and exceeds 2 % of the weight, it is not desirable. It is desirable also from an easy point to carry out the stimulus value Y of a photosensitive paste to it being the range of the further above-mentioned addition in the required range in this invention.

[0092] Although an organic system color may be mixed as one component of a photosensitive paste, the approach of processing a non-subtlety particle with a color solution, carrying out the coat of the organic dye film to a non-subtlety particle beforehand, and adding this is also effective.

[0093] An organic solvent, a sensitizer, polymerization inhibitor, a dispersant, a stabilizer, a thickener, etc. can be added to a photosensitive paste if needed other than the above-mentioned component.

[0094] Moreover, a photosensitive paste can adjust the viscosity when applying to a glass substrate with an organic solvent according to the method of application. As an organic solvent used at this time, the mixture of organic solvents containing one or more of sorts of these [ methyl cellosolve, ethylcellosolve, butyl cellosolve, a methyl ethyl ketone dioxane, an acetone, a cyclohexanone, cyclopentanone, isobutyl alcohol, isopropyl alcohol, a tetrahydrofuran, dimethyl sulfoxide, gamma-butyrolactone, etc. and ] is used.

[0095] Although paste viscosity is adjusted at an addition rate, such as a non-subtlety particle, a photosensitive organic component, an organic solvent, and other additives, the range is 10,000–200,000cps (centipoise). For example, for applying spreading to a glass substrate once with screen printing, and obtaining 10–20 micrometers of thickness, 50,000–200,000cps is desirable. When using the blade coating-machine method, the die coating-machine method, etc., 10,000–20,000cps is desirable.

[0096] With 3 rollers or a kneading machine, to homogeneity, mixed distribution can be carried out and the photosensitive paste of this invention can produce them, after preparing various components, such as for example, a non-subtlety particle, a photosensitive monomer, photosensitive oligomer or a polymer, a photopolymerization initiator, an ultraviolet ray absorbent, other additives, and a solvent, so that it may become a predetermined presentation.

[0097] The septum which presents the black made into the purpose of this invention is obtained by controlling strictly the photosensitive monomer contained in the size, the configuration, the particle size distribution and the content of the non-subtlety particle under photosensitive paste for septum pattern formation, the class, addition and the addition approach of a black pigment, and a photosensitive organic component, the class and content of a polymer, a class, an amount of an additive component, etc. with sufficient balance. Since it has delicate effect on the vaporization (debinder nature) of the organic component at the time of baking, and the description of the septum by which burning shrinkage was formed, it is necessary to choose a non-subtlety particle, a black pigment, and an organic component, and to choose baking conditions.

[0098] The photosensitive paste of this invention can be preferably used as an object for pattern formation in PDP or a plasma-address-liquid-crystal display.



[0099] Next, the manufacture approach of PDP of this invention is explained.

[0100] The non-subtlety particle whose stimulus values [ in / in the manufacture approach of PDP of this invention / the XYZ color system before baking ] Y are 20-80 and whose stimulus values Y after baking are 5-30, By applying and drying the photosensitive paste containing a photosensitive organic component on a substrate After the stimulus value Y in an XYZ color system forms the spreading film of 20-60, patterning is carried out by the photolithography method and it is characterized by calcinating this pattern and the stimulus value Y in an XYZ color system forming the septum of 2-20.

[0101] That is, after applying and drying the above-mentioned photosensitive paste on a substrate, it is the manufacture approach of PDP which carries out patterning by the photolithography method, calcinates this pattern, and forms a septum.

[0102] Septum formation by the septum pattern formation and baking using a photosensitive paste is performed as follows. First, a photosensitive paste is applied to a glass substrate. As the method of application, general approaches, such as screen printing, the bar coating-machine method, the roll coater method, the slit-die method, and a doctor blade method, can be used. Spreading thickness can be adjusted by choosing the count of spreading, the screen mesh of screen-stencil, and the viscosity of a paste.

[0103] After forming the glass substrate top which carried out surface treatment of the photosensitive paste if needed, or the dielectric layer and applying upwards, it exposes using an aligner. It is carried out through a photo mask so that exposure may be performed by the usual photolithography technique. In this case, any of the pro squeak tea exposing method which end and perform the approach or fixed spacing which sticks a photo mask to the spreading film front face of a photosensitive paste may be used. The activity beam of light used for exposure has the most desirable ultraviolet rays, and a low pressure mercury lamp, a high pressure mercury vapor lamp, an ultrahigh pressure mercury lamp, a halogen lamp, etc. are used as the light source. It is common to use a pro squeak tea exposure machine using the parallel ray which made the ultrahigh pressure mercury lamp the light source. Although exposure conditions change with spreading thickness of a photosensitive paste, exposure is performed for 0.5 - 30 minutes cm, using the ultrahigh pressure mercury lamp of the output of 2 1-100mW /.

[0104] After exposure, although negatives are developed using the solubility difference over the developer of an exposure part and an unexposed part, dip coating, a spray method, the brush method, etc. are used in this case. The solution which can dissolve the organic component especially the photosensitive oligomer, or the polymer under photosensitive paste is used for a developer. The development in an alkali water solution is attained by choosing the photosensitive oligomer or the polymer which has a carboxyl group in a side chain. Although the water solution of a sodium hydroxide, a sodium carbonate, and a calcium hydroxide etc. can be used as an alkali water solution, since the direction which used the organic alkali water solution tends to remove an alkali component at the time of baking, it is desirable. A common amine compound can be used as organic alkali. Specifically, tetramethylammonium hydroxide, trimethyl benzyl ammonium hydroxide, monoethanolamine, diethanolamine, etc. are mentioned. The concentration of an alkali water solution has 0.05 - 5 desirable % of the weight, and it is 0.1 - 1 % of the weight more preferably. If alkali concentration is too low, a fusible part will not be removed completely, but if alkali concentration is too high, there is a possibility of making exfoliating the pattern of the exposure section or eating away. As for the temperature at the time of development, it is desirable on production control to carry out at 20-50 degrees C.

[0105] The septum pattern formed through the process of exposure and development from the spreading film of a photosensitive paste is calcinated with a firing furnace next, pyrolyzes and removes an organic component, carries out melting of the glass powder in a non-subtlety particle component to coincidence, and forms an inorganic septum. Although a firing environments and temperature change with properties of a paste or a substrate, they are usually calcinated in air. As a firing furnace, the firing furnace of a batch type and the continuation mold firing furnace of a belt type can be used.

[0106] After carrying out the temperature up of the glass substrate with which the septum pattern was usually formed for calcinating a batch type at uniform velocity mostly over several hours from a room temperature to about 500 degrees C, 560-580 degrees C set up as a burning temperature are raised in 30 - 40 minutes, and it calcinates by holding for 15 - 30 minutes. Since burning temperature must be lower than the glass transition point of the glass substrate to be used, an upper limit exists naturally. Burning temperature is too high, or if firing time is too long, defects, such as sagging, will occur in the configuration of a septum. Moreover, if the pyrolysis character of the photosensitive monomer contained in an organic component, photosensitive oligomer or a polymer, and various additives and the heat characteristic of a glass powder component become disproportionate, the defect to which a septum colors it brown or a septum separates from a substrate will occur.

[0107] The stimulus values [ in / in the septum by which the stimulus value Y in the XYZ color system of this invention was formed through above-mentioned septum pattern formation and an above-mentioned baking process using the photosensitive paste which used the non-subtlety particle of 20-80 as the combination component / an XYZ color system ] Y are 2-20, and a chromaticity coordinate x and y show 0.3-0.36 further, respectively.

[0108] PDP is manufactured by being able to obtain the substrate for PDP by forming a fluorescent substance layer in the side face of the septum formed on the substrate, and the pars basilaris ossis occipitalis between septa, enclosing discharge gas, after sealing with the front-windshield substrate created separately, and mounting wiring.

[0109] Thus, obtained PDP enables the display which was excellent in contrast.

[0110]

[Example] Although an example is used for below and this invention is concretely explained to it, it is not limited to these. In addition, especially concentration (%) is weight % unless it refuses.



[0111] The presentation (analysis value) used the thing of 8.6% of lithium oxide, 20.1% of oxidization silicon, 31% of boron oxide, 3.8% of barium oxide, 20.6% of aluminum oxides, 2.1% of zinc oxides, 5.9% of magnesium oxides, and 4.2% of calcium oxides as example 1 glass powder.

[0112] The glass transition point of this glass powder was 472 degrees C, and softening temperature was 515 degrees C. The mean particle diameter of glass powder was 2.2 micrometers, and the average refractive index was 1.59.

[0113] As a filler, it consisted of 38.2% of oxidization silicon, 9.2% of boron oxide, 5.1% of barium oxide, 4.4% of calcium oxides, 34.5% of aluminum oxides, 2.1% of titanium oxide, and 4.8% of magnesium oxides, and high-melting glass of 652 degrees C of glass transition points and 746 degrees C of softening temperatures was used. The mean particle diameter of this high-melting glass was 2.5 micrometers, the maximum particle diameter was 10.0 micrometers, and the refractive index was 1.58.

[0114] As a non-subtlety particle, to 70% of glass powder, and filler component [ high-melting glass 30% of ] mixture, in total, it mixed 10% and an iron sesquioxide, cobalt oxide, and the mixed powder of chromium(III) oxide were used. The mixed rate of these black pigment component was 4:3:3 in the weight ratio. The stimulus value Y in the XYZ color system of the non-subtlety particle which carried out such combination was 45 in measurement by the color computer. Moreover, Y value of the powder after baking was 10.

[0115] 0.15% of azo system color Sudan IV (Tokyo formation product made from Industry) was dissolved in the acetone to the non-subtlety particle which consists of the high-melting glass and the black pigment powder as glass powder and a filler component, the dispersant was added and it agitated to homogeneity with the homogenizer, and the non-subtlety particle was added in this solution, after distribution / mixing and a rotary evaporator were used for homogeneity, it dried at the temperature of 150–200 degrees C, and the acetone was evaporated.

[0116] On the other hand, agitating [ mixed so that it might become a solution 40%, and ] the photosensitive polymer (X-4007) in a solvent (gamma-butyrolactone), it heated to 60 degrees C and all the polymers were dissolved in homogeneity. Subsequently, a solution is cooled to a room temperature, and 6% (IC-369) of photopolymerization initiators, 4% (1, 2, 3-benzotriazol) of stabilizers, 1% (NOPUKO sparse 092:Sannopuko make) of dispersants, and 0.14% (HQME) of polymerization inhibitor were added to 55% of this polymer solution, and it was made to dissolve in it photosensitive monomer (MGP400) 25%. Then, this solution was filtered using the filter of 400 meshes, and the organic vehicle was produced.

[0117] 3 rollers mixed and distributed the non-subtlety particle 70 weight section which contains glass powder, a filler component, and a black pigment as mentioned above to the obtained organic vehicle 65 weight section, and the photosensitive paste was prepared.

[0118] The spreading film with a desiccation thickness of 50 micrometers which applied this photosensitive paste to homogeneity by the screen-stencil which used the screen of 325 meshes on 100mm angle glass substrate was produced, and the stimulus value Y in total light transmission, the total reflection factor, a normal reflection factor, and an XYZ color system was measured. Each measurement result was as follows.

[0119]

total light transmission 35% normal permeability 30% total reflection factor 8% normal reflection factor Stimulus value Y in 20% XYZ color system 40 — this photosensitive paste was applied to multiple-times homogeneity with screen printing, and the spreading film with a desiccation thickness [ for septum pattern formation ] of 170 micrometers was produced. Whenever it applied in order to avoid generating of the pinhole of the spreading film etc., 80 degrees C and the desiccation for 10 minutes were repeated, and finally 80 degrees C and desiccation for 90 minutes were performed.

[0120] By the shape of a stripe, on this spreading film, the negative-mold chromium mask which has pitch 150micrometer and a pattern with a line breadth of 20 micrometers was set, spacing of 100 micrometers has been arranged on it, and the ultrahigh pressure mercury lamp of 20 mW/cm<sup>2</sup> output performed ultraviolet-rays exposure. Light exposure was 0.5 J/cm<sup>2</sup>.

[0121] Next, negatives were developed by pouring in a shower 0.2% of water solution of the monoethanolamine held at 35 degrees C for 90 seconds, and after that, it rinsed using the shower spray, and the tooth-space part which has not carried out photo-curing was removed, and the stripe-like septum pattern was formed on the glass substrate.

[0122] Thus, the black septum has been formed when 560 degrees C of obtained septum patterns were calcinated for 30 minutes in air. When the cross-section configuration of the formed septum was observed with the electron microscope, it was height [ of 120 micrometers ], line breadth [ of a septum crowning / of 30 micrometers ], and pitch 150micrometer. The stimulus value Y in the XYZ color system of the septum layer measured using the sample which calcinated the solid film previously used in order to measure the property of the photosensitive paste coating film was 5.5.

[0123] The fluorescent substance layer was applied between the septa on the substrate with which the electrode, the dielectric layer, and the black septum were formed, and it sealed together with the front plate, and gas charging was carried out, the drive circuit was connected, and the plasma display was produced. It displayed on this panel by impressing an electrical potential difference. The contrast ratio was measured from the brightness at the time of complete lighting, and the reflection factor at the time of putting out lights. The contrast ratio was measured using photometry opportunity MCPD-200 (Otsuka electronic company make). The contrast ratio was excellent with 200:1.

[0124] Although example 2 example 1 was repeated, the ultraviolet ray absorbent to be used was made into the benzophenone system compound 2 and 4-dihydroxy benzophenone, and 0.12% was used to the non-subtlety particle.

The stimulus value Y in the total light transmission, the total reflection factor, normal reflection factor, and XYZ color system of a photosensitive paste in this case was as follows.

[0125]

total light transmission 42% normal permeability 30% total reflection factor 8% normal reflection factor Stimulus value Y in 26% XYZ color system 35 — the septum was formed like the example 1 using the photosensitive paste coating film which has such a property. The stimulus value Y in the XYZ color system of the obtained septum was 12.

[0126] Although example 3 example 1 was repeated, cordierite (the mean particle diameter of 2 micrometers, refractive index 1.56) was used instead of high-melting glass as a filler component. The stimulus value Y in the XYZ color system of the non-subtlety particle in this case was 50. Moreover, Y value of the powder after baking was 25.

[0127] The stimulus value Y in the total light transmission, the total reflection factor, normal reflection factor, and XYZ color system of the paste obtained when this non-subtlety particle was applied to a photosensitive paste like an example 1 was as follows.

[0128]

total light transmission 45% normal permeability 32% total reflection factor 7.5% normal reflection factor Stimulus value Y in 28% XYZ color system 30 — the septum was formed like the example 1 using the photosensitive paste coating film which has such a property. The stimulus value Y in the XYZ color system of the obtained septum was 18.

[0129] It has the presentation of 6.4% of lithium oxide, 15% of oxidization silicon, 36% of boron oxide, 20% of aluminum oxides, 3.9% of barium oxide, 3.9% of magnesium oxides, 3.4% of calcium oxides, and 8.1% of zinc oxides, by the example tetroxide conversion presentation, melting mixing was carried out so that it might become a total of 15% about an iron sesquioxide, cobalt oxide, and chromium(III) oxide at a rate of 4:3:3 by the oxide equivalent weight ratio in the creation phase the glass powder of 477 degrees C of glass transition points, and 521 degrees C of softening temperatures, and the glass powder containing a black pigment component be created. The alumina (mean-particle-diameter [ of 2.5 micrometers ], refractive index 1.77) 20 weight section was mixed as a filler in this glass powder 80 weight section, and the non-subtlety particle was obtained. The stimulus value Y in the XYZ color system of a non-subtlety particle was 30. Moreover, Y value of the powder after baking was 20.

[0130] The photosensitive paste was produced like the example 1 using this non-subtlety particle. However, they are Uvinul3039 (BASF Japan make) 0.5% and the BASIC blue 7 as an ultraviolet ray absorbent. 0.05% (all receiving a non-subtlety particle) was used, and these were mixed and used for the photosensitive paste as an organic component. The stimulus value Y in the total light transmission measured about this photosensitive paste, the total reflection factor, a normal reflection factor, and an XYZ color system was as follows.

[0131]

total light transmission 60% normal permeability 45% total reflection factor 8% normal reflection factor Stimulus value Y in 32% XYZ color system 42 — the septum was formed like the example 1 using the photosensitive paste coating film which has such a property. The stimulus value Y in the XYZ color system of the obtained septum was 15.

[0132] The example 4 was repeated for the mixed ratio of the glass powder and the filler component which contain a black pigment component as a non-subtlety particle in example 5 example 4 as 85 weight sections and the 15 weight sections, respectively. The stimulus value Y in the XYZ color system of a non-subtlety particle was 38.

Moreover, Y value of the powder after baking was 18. The stimulus value Y in the total light transmission, the total reflection factor, normal reflection factor, and XYZ color system of the photosensitive paste using this non-subtlety particle was as follows.

[0133]

total light transmission 55% normal permeability 60% total reflection factor 8% normal reflection factor Stimulus value Y in 25% XYZ color system 32 — the septum was formed like the example 1 using the photosensitive paste coating film which has such a property. The stimulus value Y in the XYZ color system of the obtained septum was 12.

[0134] The example 4 was repeated for the mixed ratio of the glass powder and the filler component which contain a black pigment component as a non-subtlety particle in example 6 example 4 as 65 weight sections and the 35 weight sections, respectively. The stimulus value Y in the XYZ color system of a non-subtlety particle was 50.

Moreover, Y value of the powder after baking was 14.

[0135] The stimulus value Y in the total light transmission, the total reflection factor, normal reflection factor, and XYZ color system of the photosensitive paste using this non-subtlety particle was as follows.

[0136]

total light transmission 65% normal permeability 55% total reflection factor 7% normal reflection factor Stimulus value Y in 55% XYZ color system 24 — the septum was formed like the example 1 using the photosensitive paste coating film which has such a property. The stimulus value Y in the XYZ color system of the obtained septum was 8.

[0137] In example 7 example 4, the glass powder which carried out melting mixing of the black pigment component so that it might become 10% in total about a content was produced, and the example 4 was repeated except using it. The stimulus value Y in the XYZ color system of a non-subtlety particle was 60. Moreover, Y value of the powder after baking was 20.

[0138] The stimulus value Y in the total light transmission, the total reflection factor, normal reflection factor, and XYZ color system of the photosensitive paste using this non-subtlety particle was as follows.

[0139]

total light transmission 65% normal permeability 50% total reflection factor 8% normal reflection factor Stimulus value Y in 42% XYZ color system 55 — the septum was formed like the example 1 using the photosensitive paste coating

film which has such a property. The stimulus value Y in the XYZ color system of the obtained septum was 13.

[0140] In example 8 example 1, the example 1 was repeated except using nickel oxide and cobalt oxide (oxide equivalent weight ratio 1:1) 10% of the weight in total as a black pigment to add.

[0141] The stimulus value Y in the XYZ color system of a non-subtlety particle was 31. Moreover, Y value of the powder after baking was 15.

[0142] The stimulus value Y in the total light transmission, the total reflection factor, normal reflection factor, and XYZ color system of the photosensitive paste using this non-subtlety particle was as follows.

[0143]

total light transmission 55% normal permeability 35% total reflection factor 6.5% normal reflection factor Stimulus value Y in 25% XYZ color system 28 — the septum was formed like the example 1 using the photosensitive paste coating film which has such a property. The stimulus value Y in the XYZ color system of the obtained septum was 10.

[0144] It has the presentation of 6.7% of lithium oxide, 22% of oxidization silicon, 32% of boron oxide, 19% of aluminum oxides, 3.9% of barium oxide, 5.5% of magnesium oxides, 4.1% of calcium oxides, and 5.5% of zinc oxides, as example 9 glass powder, melting mixing was carried out so that it might become a total of 15% about an iron sesquioxide, cobalt oxide, and chromium(III) oxide at a rate of 4:3:3 by the oxide equivalent weight ratio in the creation phase the glass powder of 497 degrees C of glass transition points and 530 degrees C of softening temperatures, and the glass powder containing a black pigment component be created. The alumina (mean-particle-diameter [ of 2.5 micrometers ], refractive index 1.77) 20 weight section was mixed as a filler in this glass powder 80 weight section, and the non-subtlety particle was obtained. The stimulus value Y in the XYZ color system of a non-subtlety particle was 30. Y value of the powder after baking was 12.

[0145] The photosensitive paste was produced like the example 4. The stimulus value Y in the total light transmission, the total reflection factor, normal reflection factor, and XYZ color system of a photosensitive paste was as follows.

[0146]

total light transmission 55% normal permeability 45% total reflection factor 7% normal reflection factor Stimulus value Y in 33% XYZ color system 26 — the septum was formed like the example 1 using the photosensitive paste coating film which has such a property. The stimulus value Y in the XYZ color system of the obtained septum was 7.

[0147] As example of comparison 1 black pigment, the same experiment as an example 1 was repeated except having used nickel oxide and cobalt oxide (oxide equivalent weight ratio 2:1) 6% in total. The stimulus value Y in the XYZ color system of the obtained non-subtlety particle was before and after baking, and were 60 and 40, respectively.

[0148] Next, the spreading film was produced like the example 1 and the stimulus value Y in total light transmission, the total reflection factor, a normal reflection factor, and an XYZ color system was measured. Each measurement result was as follows.

[0149]

Total light transmission 75% normal permeability 60% total reflection factor 7% normal reflection factor Stimulus value Y in 52% XYZ color system The stimulus value Y in the XYZ color system of the solid film for 30 minutes and after baking was 35 at 55, next 560 degrees C. Moreover, when the contrast ratio of a plasma display was measured, it was as low as 30:1.

[0150] As example of comparison 2 black pigment, what mixed cobalt oxide, chrome oxide (III), and an iron sesquioxide (oxide equivalent weight ratio 2.7:3.3:5) 11% in total was used.

[0151] Next, when the stimulus value Y in the XYZ color system of the non-subtlety particle before and behind baking was measured like the example 1, it was 18 and 11, respectively.

[0152] Next, the spreading film was produced like the example 1 and the stimulus value Y in total light transmission, the total reflection factor, a normal reflection factor, and an XYZ color system was measured. Each measurement result was as follows.

[0153]

Total light transmission 1.5% normal permeability 0.2% total reflection factor 8% normal reflection factor Stimulus value Y in 0.4% XYZ color system Although septum pattern formation was tried like 15, next an example 1, in order for light not to arrive and not to carry out photo-curing to the septum layer lower part, it dissolved in the developer at the time of development. For this reason, pattern formation was not able to be carried out.

[0154] To the same glass constituent as example of comparison 3 example 9, as a black pigment, as it became 2.5% in total, melting mixing of nickel oxide and the cobalt oxide (oxide equivalent weight ratio 1:1) was carried out like the example 9, and the glass powder containing a black pigment component was produced. Y values in the XYZ color system of the glass powder before and behind baking were 85 and 45, respectively. Next, the photosensitive paste was produced like the example 4 and the stimulus value Y in total light transmission, the total reflection factor, a normal reflection factor, and an XYZ color system was measured. Each measurement result was as follows.

[0155]

Total light transmission 70% normal permeability 65% total reflection factor 10% normal reflection factor Stimulus value Y in 55% XYZ color system The stimulus value Y in the XYZ color system of the solid film for 30 minutes and after baking was 30 at 70, next 560 degrees C. Moreover, when the contrast ratio of a plasma display was measured, it was as low as 40:1.

[0156] Explanation of an abridged notation: Photosensitive polymer of the weight average molecular weight 43 and

000 to which the addition reaction of the 0.4Eq glycidyl methacrylate was carried out to X-4007:40% methacrylic acid, 30% methyl methacrylate, and the carboxyl group of the copolymer which consists of styrene 30%, and the acid number 95.

[0157]

MGP400:X2 N-CH(CH<sub>3</sub>)-CH<sub>2</sub>-(OCH<sub>2</sub>CH(CH<sub>3</sub>))<sub>n</sub>-NX<sub>2</sub> — here — X=-CH<sub>2</sub>CH(OH)-CH<sub>2</sub> O-CO-C(CH<sub>3</sub>)=CH<sub>2</sub>n=2-10IC-369:Irgacure369 (Ciba-Geigy product)

2-benzyl-2-dimethylamino-1-(4-morpholino phenyl) butanone-1HQME: Hydroquinone monomethyl ether [0158]

[Effect of the Invention] The non-subtlety particle of this invention is a non-subtlety particle for a photosensitive paste, and the stimulus values Y in the XYZ color system before baking are 20-80, and the stimulus values Y after baking are 5-30. Moreover, the stimulus values Y in an XYZ color system when the photosensitive paste which consists of this non-subtlety particle and a photosensitive organic component forms the spreading film with a thickness of 50 micrometers are 20-60, and the stimulus value Y after calcinating this spreading film is set to 2-20. For this reason, in the condition of the paste coating film, it excels in the reflection factor on light transmission nature or the front face of a paint film, and a good pattern can be formed, without repeating an exposure process. Moreover, a black septum can be formed if a septum pattern is calcinated. For this reason, PDP whose contrast improved can be easily manufactured with the photolithography technique in which a high aspect ratio and high definition septum formation are possible.

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[Translation done.]